



# Synthesis, structure, and quaternization and complexation reactions of 3SCS pincer palladium complexes having 3,5-pyridinediyl unit

著者	Meguro Hikaru, Koizumi Take-aki, Yamamoto Takakazu, Kanbara Takaki
journal or publication title	Journal of organometallic chemistry
volume	693
number	6
page range	1109-1116
year	2008-03
権利	(C) 2008 Elsevier B.V.
URL	<a href="http://hdl.handle.net/2241/98624">http://hdl.handle.net/2241/98624</a>

doi: 10.1016/j.jorganchem.2007.12.033

# Synthesis, Structure, and Quaternization and Complexation Reactions of $\kappa^3$ SCS Pincer Palladium Complexes Having 3,5-Pyridinediyl Unit

Hikaru Meguro<sup>a</sup>, Take-aki Koizumi<sup>a</sup>, Takakazu Yamamoto<sup>a</sup>, and Takaki Kanbara<sup>b,c,\*</sup>

<sup>a</sup> Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

<sup>b</sup> Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

<sup>c</sup> Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

Corresponding author.

Tel.: +81-29-853-5066; fax: +81-29-853-4490; E-mail: kanbara@ims.tsukuba.ac.jp

## Abstract

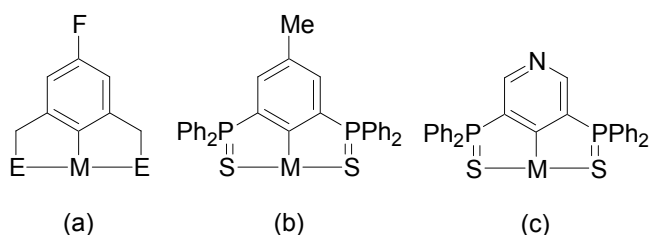
The cyclopalladation of 3,5-bis(diphenylphosphinothioyl)pyridine afforded new  $\kappa^3$ S,C,S-pincer palladium complexes with a  $\sigma$ -bond between Pd and 4-C of the centered 3,5-pyridinediyl unit. By utilizing the quaternization and complexation ability of the pyridine imine nitrogen ( $N_{py}$ ) atom, various new pincer-type complexes, including hetero-binuclear complexes, have been synthesized.

Keywords: pincer complex; palladium; pyridine; quaternization; binuclear complexes

## 1. Introduction

Pincer palladium complexes have been intensively investigated in the field of catalysis and material science [1]. Self-assembled metallocupramolecules have also been the subject of recent interest [2,3]. To construct metallocupramolecules of pincer complexes, the introduction of several functional groups at the *para*-position of the centered arene ring of pincer ligands (e.g., the pincer complex with structure (a) in Scheme

1) has been achieved [1a,1b,3]. Recently, pincer complexes attached to terpyridine and porphyrin units have also been synthesized, and their interesting chemical properties have been revealed [3k,3l,3r].



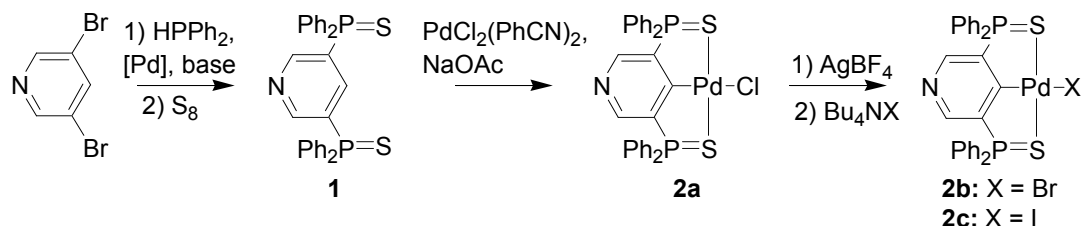
**Scheme 1.** Pincer complexes: E = chelating donor atom; F = Functional or coordinating substituent.

We previously reported the preparation of pincer palladium complexes with a centered phenylene-type ligand bearing phosphine sulfide auxiliary ligands at the *o*-positions (cf. molecular formula (b) in Scheme 1) [4]. As an extension of the research, we have prepared new pincer complexes of type (c) depicted in Scheme 1. Replacing the centered phenylene unit in the pincer ligand by a pyridine unit offers interesting possibilities. The presence of a reacting and coordinating pyridine imine nitrogen ( $N_{py}$ ) atom will make it possible to create various new pincer complexes derived from the complex of type (c). Examples of such pincer ligands with a 3,5-pyridinediyl moiety, however, have been limited [5], because the presence of  $N_{py}$  sometimes leads to a number of unexpected coordination modes [5b]. Milstein *et al.* successfully demonstrated that  $\kappa^3P,C,P$ -pincer rhodium and palladium complexes of a monoanionic bis(phosphine)pyridine ligand,  $[3,5-(Ph_2PCH_2)_2C_5H_2N]^-$ , serve as a metalloligand for a second metal center [5a]. We herein report the synthesis of a new pincer complex of type (c) and the quaternization and complexation reactions of the pincer complex.

## 2. Results and Discussion

The Pd-catalyzed aryl phosphination of 3,5-dibromopyridine with two equivalents of diphenylphosphine followed by sulfurization with elemental sulfur afforded ligand **1**, as shown in Scheme 2 [4,6]. The pincer palladium complex **2a** was obtained via the *ortho,ortho*-cyclopalladation of **1** with  $PdCl_2(PhCN)_2$ . The addition of sodium acetate led to regioselective cyclopalladation at the 4-C position of the centered pyridine

ring. The treatment of **2a** with AgBF<sub>4</sub> followed by the addition of Bu<sub>4</sub>NX (X = Br, I) gave the corresponding bromo- (**2b**) and iodo- (**2c**) complexes.

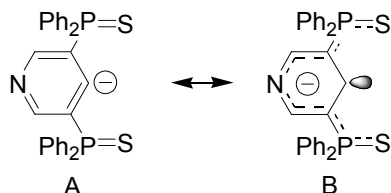


**Scheme 2.**

The chemical structures of **1** and **2a-c** were confirmed by NMR, FAB-mass spectroscopy, and elemental analysis. In the <sup>1</sup>H NMR spectrum of **2a**, the signal assigned to the 4-H of the centered pyridine ring disappeared, and an upfield shift (0.15 ppm) of the signal, assigned to the 2,6-H of the pyridine ring, was observed. The cyclopalladation led to a downfield shift of the <sup>13</sup>C NMR signal of C<sub>ipso</sub> by 37 ppm due to the σ-bonding to Pd. The <sup>31</sup>P NMR spectrum of **2a** exhibited a downfield shift of the signal by 16 ppm due to the S-coordination mainly, and the two phosphine sulfide groups were magnetically equivalent in the complex. Evidence of S-coordination was also supported by the ν(P=S) position of **2a** (603 cm<sup>-1</sup>), which appeared at a lower frequency than that of **1** (645 cm<sup>-1</sup>).

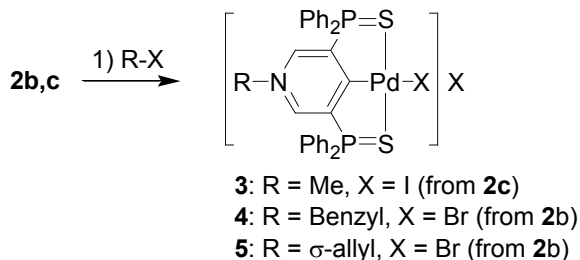
The ORTEP drawings of **1** and **2a** are presented in Figure 1. Detailed results of X-ray crystallography and selected bond lengths are summarized in Tables 1 and 2, respectively. **2a** has a distorted square-planar geometry, and the Pd-C, Pd-S, and Pd-Cl bond lengths lie within the range of lengths found in related pincer palladium complexes [4]. The P=S bond lengths of **2a** (2.003(3) and 2.012(3) Å) are somewhat longer, while the P-C bond lengths of the phosphine sulfide and the centered pyridine ring in **2a** (1.810(9) and 1.793(7) Å) are shorter than those of **1** (P-S, 1.9460(10) Å; P-C, 1.814(2) Å). A similar structural feature was observed for **2b** and **2c**; the ORTEP drawings and detailed results of X-ray crystallography of **2b** and **2c** are given in Supplementary material. These data suggest that the cyclopalladation leads to the delocalization of electrons within the unsaturated part of the ligand, as shown in **B** in Scheme 3. A similar suggestion has been made for

$\kappa^3$ S,P,S-pincer complexes composed of a phosphinine ring bearing two phosphine sulfide side arms [7].

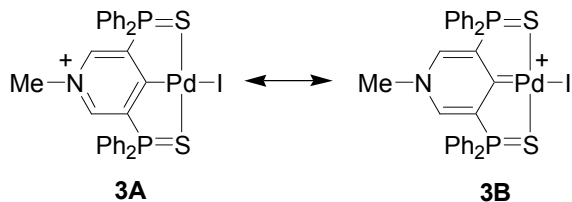


**Scheme 3.** Delocalization of electron in the pincer ligand.

The treatment of **2b** and **2c** with alkylhalides afforded N<sub>py</sub>-quaternized pyridinium complexes **3-5**. The <sup>1</sup>H NMR spectra of **3-5** were consistent with their molecular structures. The <sup>13</sup>C NMR spectra of **3-5** showed the Pd-C<sub>ipso</sub> signal at a considerably lower field ( $\delta$  212-206) than those of **2b** and **2c** ( $\delta$  186 for **2b** and  $\delta$  191 for **2c**). The Pd-C<sub>ipso</sub> signal position was at a lower magnetic field than those of related Pd-pyridinium/pyridinylidene complexes ( $\delta$  178-190) [8] and similar to those of Pd-quinolin-4-ylidene complexes with a C=Pd<sup>+</sup> bond ( $\delta$  208-201) [9]. Consequently, the NMR spectra of **3-5** are considered to have a contribution from the resonance structure such as **3B** in Scheme 5.



**Scheme 4**

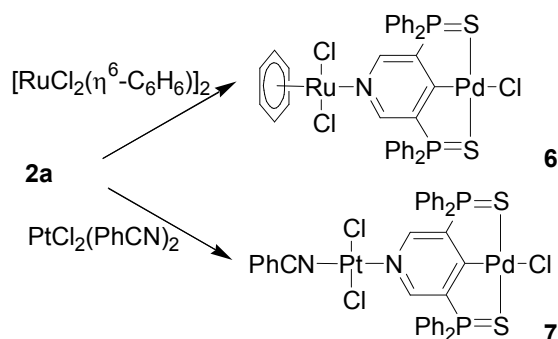


**Scheme 5**

X-ray quality single crystals of **3** and **5** were obtained from their ion exchange with NH<sub>4</sub>PF<sub>6</sub> to give hexafluorophosphate salts, **3'** and **5'**, respectively. Figure 2 shows the ORTEP drawings of **3'** and **5'**. Detailed

results of X-ray crystallography and selected bond lengths are shown in Tables 1 and 2, respectively. The Pd-C<sub>ipso</sub> bond lengths of **3'** (1.994(6) Å) and **5'** (1.994(5) Å) are slightly shorter than those of **2c** (2.005(5) Å) and **2b** (2.006(11) Å), respectively. The bond lengths are comparable to those of the reported Pd-pyridinium/pyridinylidene complexes [8b,8c] and the Pd-quinolin-4-ylidene complexes with a C=Pd<sup>+</sup> bond [9]. Raubenheimer *et al.* reported that there is little difference between a Pd-quinolin-6-ylidene complex and a Pd-quinolin-6-yl complex in terms of the Pd-C bond lengths [10].

The coordinating ability of the N<sub>py</sub> atom of **2a** allowed the binding of **2a** to other metal centers. The reactions of **2a** with [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)]<sub>2</sub> and [PtCl<sub>2</sub>(PhCN)]<sub>2</sub> led to the formation of hetero-binuclear complexes, **6** and **7**, respectively, as exhibited in Scheme 6.



**Scheme 6.**

In the <sup>1</sup>H NMR spectra of **6** and **7**, the 2,6-H signal of the pyridine ring showed respective downfield shifts of 0.42 and 0.24 ppm from that of **2a**. For **6**, the signal of H at η<sup>6</sup>-benzene was observed at δ 5.43.

The ORTEP drawing of **6** is presented in Figure 3. The molecular structure reveals that the Ru(II) center of **6** is located in a piano-stool conformation, and the pincer fragment of **6** maintains the same geometry, with bond lengths and angles essentially similar to those of **2a**, as shown in Table 2. The Ru-N<sub>py</sub> bond length (N<sub>py</sub>-Ru = 2.152(8) Å) falls within the range reported for related complexes such as [RuCl<sub>2</sub>(η-1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)(pyridine)] [11]. These results indicate that **2a** serves as an N<sub>py</sub>-coordinating metalloligand and does not change the basic structure of the connecting metal complexes upon coordination.

UV-vis absorption data for the complexes are summarized in Table 3, and the spectra are shown in

Figure S2. **2-5** have absorption bands in the region of 350–470 nm, and the shape of the spectra in the region is similar to that of reported pincer palladium complexes such as [3,5-bis(diphenylphosphinothioyl)toluene-C<sup>4</sup>,S,S']chloropalladium(II) (**8**, cf. Scheme 1(b)), in which the absorption bands have been tentatively assigned to a metal-to-ligand charge-transfer (MLCT) transition [4a]. The absorption band of **2a** is observed in an energy region that is about 20 nm lower than that of **8**, suggesting that replacing the centered phenylene unit in the pincer ligand by a pyridine unit resulted in a reduction in the energy level of the  $\pi^*$  orbital of the ligand. For complexes **2a** (X = Cl,  $\lambda_{\text{max,MLCT}}$  = 346 nm), **2b** (X = Br,  $\lambda_{\text{max,MLCT}}$  = 352 nm), and **2c** (X = I,  $\lambda_{\text{max,MLCT}}$  = 392 nm), the peak position shifts in the lower-energy direction with magnitude in the order of Cl > Br > I; these data suggest that an enhancement in the  $\sigma$ -donor characteristic of the halide ligand stabilizes the excited states [12]. The  $\lambda_{\text{max,MLCT}}$  of the quaternized complexes **3** (R = Me, X = I), **4** (R = CH<sub>2</sub>Ph, X = Br), and **5** (R = CH=CH<sub>2</sub>, X = Br) is observed at 405, 367, and 363 nm, respectively, which is shifted to longer wavelength by about 20 nm than those of the iodide complex **2c** and the bromide complex **2b**. These results indicate that N<sub>py</sub>-alkylation causes a bathochromic shift in the MLCT band. The electron-withdrawing substitution resulted in a reduction in the  $\pi^*$  level, and the bathochromic shift suggested that the N<sub>py</sub>-alkylation slightly affects the electron density of the metal [5a,c]. For the N<sub>py</sub>-coordination (**6** and **7**), only a slight shift in the band was observed, and the complexes exhibited absorption profiles with long tails. **8** was light-emissive in the glassy frozen state ( $\lambda_{\text{em}}$  = 590 nm,  $\phi_f$  = 0.14,  $\tau$  = 240  $\mu$ s) [4], whereas **2a** exhibited only weak emission in the glassy frozen state ( $\lambda_{\text{em}}$  = 607 nm,  $\phi_f$  = 0.01); the quaternization and coordination reactions of **2a** did not improve the emission ability.

As described above, new pincer Pd complexes **2** with a pyridine moiety have been prepared. Because of the quaternizing and coordinating reactivity of N<sub>py</sub> in **2**, these complexes are considered to be starting complexes for the formation of various pincer complexes. The preparation of a variety of hetero-binuclear pincer complexes would be of interest because there have recently been extensive studies on the catalytic reactions using the pincer palladium complexes [1].

### 3. Experimental

#### General procedure.

NMR spectra were recorded on JEOL JNM-EX-400 and Lambda-300 NMR spectrometer. Mass spectra were recorded on JEOL JMS-700 and Shimadzu LCMS-2010 Mass spectrometer. IR spectra were recorded on a JASCO FTIR-460Plus spectrometer. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 and a Yanaco SX-Elements Micro Analyzer YS-10. UV-visible absorption spectra and emission spectra were recorded on a Shimadzu UV-2550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Dichlorobis(benzonitrile)palladium,  $\text{PdCl}_2(\text{PhCN})_2$  [13] and dichlorobis(benzonitrile)platinum,  $\text{PtCl}_2(\text{PhCN})_2$  [14] were prepared according to literatures. Benzeneruthenium(II) chloride dimer,  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)]_2$ , was purchased and used as received.

#### Synthesis of 3,5-bis(diphenylphosphinothiopyridine)pyridine (1).

A mixture of 3,5-dibromopyridine (1.42 g, 6 mmol) and diphenylphosphine (2.79 g, 15 mmol) was dissolved in DMF (20 mL). Palladium chloride (53 mg, 0.3 mmol) and sodium acetate (1.48 g, 18 mmol) were added to the solution, and the reaction mixture was stirred at 130 °C for 24 h under  $\text{N}_2$ . After cooling to room temperature, sulfur (480 mg, 15 mmol as elemental sulfur) was added and the reaction mixture was stirred at 120 °C for 4 h under  $\text{N}_2$ . After cooling to room temperature, an aqueous solution of EDTA-2Na (100 mL) and  $\text{CHCl}_3$  (200 mL) were added, and the mixture was stirred for 30 min. The organic phase was separated and the solvent was evaporated. The crude product was purified by column chromatography and recrystallization from THF to give **1** as a white powder (1.96 g, 64% yield). FAB-mass:  $m/z = 512$   $[\text{M}+\text{H}]^+$ .  $^1\text{H}$  NMR (400 MHz in  $\text{CDCl}_3$ ):  $\delta$  8.96 (ddd,  $J = 6.8$  Hz, 2.3 Hz, 1.2 Hz, 2H), 8.19 (tt,  $J = 12.5$  Hz, 2.0 Hz, 1H), 7.68-7.58 (m, 8H), 7.56-7.48 (m, 4H), 7.46-7.38 (m, 8H).  $^{13}\text{C}$  NMR (100 MHz in  $\text{CDCl}_3$ ):  $\delta$  154.5 (d,  $J = 12.3$  Hz), 142.9 (d,  $J = 9.1$  Hz), 132.1, 132.0 (d,  $J = 11.5$  Hz), 131.1 (d,  $J = 85.8$  Hz), 129.9 (dd,  $J = 79.2$  Hz, 4.0 Hz), 128.8 (d,  $J = 13.3$  Hz).  $^{31}\text{P}$  NMR (160 MHz in  $\text{CDCl}_3$ ):  $\delta$  39.2. Anal. Calcd for  $\text{C}_{29}\text{H}_{23}\text{NP}_2\text{S}_2$ : C, 68.09; H, 4.53; N, 2.74; S, 12.54. Found:



C, 67.90; H, 4.73; N, 2.89; S, 12.12.

**Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C<sup>4</sup>,S,S']chloropalladium(II) (2a).**

A mixture of **1** (256 mg, 0.5 mmol), PdCl<sub>2</sub>(PhCN)<sub>2</sub> (270 mg, 0.7 mmol), and sodium acetate (123 mg, 1.5 mmol) in 1,1,2,2-tetrachloroethane (30 mL) was stirring at 150 °C for 24 h under N<sub>2</sub>. The resulting yellow precipitate was filtered and washed with hexane, ether, methanol, and water. The product was purified by recrystallization from a mixture of CHCl<sub>3</sub> and hexane to give a yellow powder of **2a** (88 mg, 27% yield). FAB-mass:  $m/z$  = 616 [M-Cl]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>): δ 8.04 (dd,  $J$  = 3.4 Hz, 2.8 Hz, 2H), 7.87-7.76 (m, 8H), 7.68-7.61 (m, 4H), 7.60-7.50 (m, 8H). <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>): δ 180.0, 150.9 (d,  $J$  = 18.5 Hz), 145.7 (dd,  $J$  = 102.4 Hz, 13.3 Hz), 133.4, 132.4 (d,  $J$  = 12.0 Hz), 129.3 (d,  $J$  = 13.3 Hz), 128.1 (d,  $J$  = 81.8 Hz). <sup>31</sup>P NMR (160 MHz in CDCl<sub>3</sub>): δ 55.4. Anal. Calcd for C<sub>29</sub>H<sub>22</sub>ClNP<sub>2</sub>PdS<sub>2</sub>: C, 53.39; H, 3.40; N, 2.15; S, 9.83. Found: C, 53.33; H, 3.24; N, 2.20; S, 9.66.

**Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C<sup>4</sup>,S,S']bromopalladium(II) (2b).**

To a THF (1 mL) solution of **2a** (9.8 mg, 0.015 mmol) was added AgBF<sub>4</sub> (5.0 mg, 0.026 mmol), and an addition of Bu<sub>4</sub>NBr (32 mg, 0.1 mmol) led to precipitation of the product. The precipitate was filtered and washed with methanol and water. The product was purified by recrystallization from a mixture of CHCl<sub>3</sub> and hexane to give a yellow powder of **2b** (5.1 mg, 49% yield). FAB-mass :  $m/z$  = 616 [M-Br]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>): δ 8.08 (dd,  $J$  = 3.3 Hz, 3.0 Hz, 2H), 7.86-7.76 (m, 8H), 7.68-7.62 (m, 4H), 7.59-7.52 (m, 8H). <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>): δ 186.0, 150.9 (d,  $J$  = 18.6 Hz), 145.1 (dd,  $J$  = 102.1 Hz, 13.3 Hz), 133.4, 132.4 (d,  $J$  = 11.9 Hz), 129.3 (d,  $J$  = 11.9 Hz), 128.2 (d,  $J$  = 81.2 Hz). <sup>31</sup>P NMR (160 MHz in CDCl<sub>3</sub>): δ 59.8. Anal. Calcd for C<sub>29</sub>H<sub>22</sub>BrNP<sub>2</sub>PdS<sub>2</sub>: C, 49.98; H, 3.18; N, 2.01; S, 9.20. Found: C, 50.02; H, 3.21; N, 1.98; S, 9.23.

**Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C<sup>4</sup>,S,S']iodopalladium(II) (2c).**

Similar procedure described above was adopted using Bu<sub>4</sub>NI (37 mg, 0.1 mmol) to give **2c** (5.7 mg, 52% yield). FAB-mass :  $m/z$  = 616 [M-I]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>): δ 8.18 (dd,  $J$  = 3.1 Hz, 3.0 Hz, 2H), 7.83-7.72 (m, 8H), 7.66-7.60 (m, 4H), 7.57-7.50 (m, 8H). <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>): δ 190.7, 150.6 (d,  $J$  = 18.5 Hz),

143.8 (dd,  $J = 102.0$  Hz, 13.9 Hz), 133.4, 132.3 (d,  $J = 11.9$  Hz), 129.4 (d,  $J = 11.9$  Hz), 128.2 (d,  $J = 79.8$  Hz).

$^{31}\text{P}$  NMR (160 MHz in  $\text{CDCl}_3$ ):  $\delta$  68.6. Anal. Calcd for  $\text{C}_{29}\text{H}_{22}\text{INP}_2\text{PdS}_2$ : C, 46.82; H, 2.98; N, 1.88; S, 8.62.

Found: C, 49.55; H, 3.20; N, 1.88; S, 8.58.

**Synthesis of [N-methyl-3,5-bis(diphenylphosphinothioyl)pyridinium- $\text{C}^4,\text{S},\text{S}'$ ] iodopalladium(II) iodide (3).**

To a THF (2 mL) solution of **2c** (9.7 mg, 0.013 mmol) was added  $\text{CH}_3\text{I}$  (1 mL) and refluxed for 6 h. The solvent was evaporated, and the residue was washed with  $\text{CHCl}_3$ , acetone and water. The product was purified by recrystallization from a mixture of  $\text{CH}_3\text{CN}$  and ether to give a yellow powder of **3** (7.4 mg, 64% yield).

ESI-mass:  $m/z = 758$   $[\text{M-I}]^+$ .  $^1\text{H}$  NMR (400 MHz in  $\text{CD}_3\text{CN}$ ):  $\delta$  8.23 (dd,  $J = 4.8$  Hz, 2.2 Hz, 2H), 7.93-7.80 (m, 12H), 7.73-7.66 (m, 8H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  206.3, 144.8 (d,  $J = 26.6$  Hz), 144.4 (dd,  $J = 107.8$  Hz, 15.9 Hz), 134.5, 132.5 (d,  $J = 11.9$  Hz), 129.8 (d,  $J = 13.3$  Hz), 125.9 (d,  $J = 80.9$  Hz), 47.6.  $^{31}\text{P}$  NMR (160 MHz in  $\text{CD}_3\text{CN}$ ):  $\delta$  67.5. Anal. Calcd for  $\text{C}_{30}\text{H}_{25}\text{I}_2\text{NP}_2\text{PdS}_2$ : C, 40.68; H, 2.84; N, 1.58.

Found: C, 39.73; H, 2.92; N, 1.50.

X-ray quality single crystals of **3** were obtained from ion exchange of **3** with  $\text{NH}_4\text{PF}_6$  to give the hexafluorophosphate salt of **3** (**3'**).

**Synthesis of [N-benzyl-3,5-bis(diphenylphosphinothioyl)pyridinium- $\text{C}^4,\text{S},\text{S}'$ ] bromopalladium(II) bromide (4).**

To a THF (5 mL) solution of **2b** (9.1 mg, 0.013 mmol) was added benzyl bromide (1 mL) and refluxed for 12 h. The solvent was evaporated, and the residue was washed with hexane, ether and water. The product was purified by recrystallization from a mixture of  $\text{CH}_3\text{CN}$  and ether to give a yellow powder of **4** (8.7 mg, 77% yield).

ESI-mass :  $m/z = 787$   $[\text{M-Br}]^+$ . HRMS: calcd for  $\text{C}_{36}\text{H}_{29}\text{NBrP}_2\text{PdS}_2$ : 787.9434. Found: 787.9395.

$^1\text{H}$  NMR (400 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  9.18 (d,  $J = 7.3$  Hz, 2H), 7.98-7.90 (m, 8H), 7.88-7.70 (m, 4H), 7.78-7.68 (m, 8H), 7.33 (m, 5H), 5.60(s, 2H).  $^{13}\text{C}$  NMR (100 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  207.1, 146.7 (dd,  $J = 107.8$  Hz, 15.9 Hz), 144.2 (d,  $J = 26.6$  Hz), 134.5, 132.6 (d,  $J = 11.9$  Hz), 129.7 (d,  $J = 13.3$  Hz), 128.9, 128.8, 128.5, 127.8, 125.8 (d,  $J = 82.5$  Hz), 62.6.  $^{31}\text{P}$  NMR (160 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  62.9.

**Synthesis of [N-allyl-3,5-bis(diphenylphosphinothioyl)pyridinium-C<sup>4</sup>,S,S']- bromopalladium(II) bromide (5).**

Similar reaction described above was carried out using **2b** and allyl bromide to give **5** (6.8 mg, 64% yield).

ESI-mass :  $m/z = 738$  [M-Br]<sup>+</sup>. HRMS: calcd for C<sub>32</sub>H<sub>27</sub>NBrP<sub>2</sub>PdS<sub>2</sub>: 737.9276. Found: 737.9210. <sup>1</sup>H NMR (400 MHz in DMSO-d<sub>6</sub>): δ 9.03 (d,  $J = 5.6$  Hz, 2H), 8.00-7.80 (m, 12H), 7.78-7.64 (m, 8H), 5.95-6.05 (m, 1H), 5.26 (d,  $J = 11.0$  Hz, 1H), 5.22 (d,  $J = 18.0$  Hz, 1H), 5.02 (s, 2H). <sup>13</sup>C NMR (100 MHz in DMSO-d<sub>6</sub>): δ 211.7, 146.3 (dd,  $J = 105.1$  Hz, 14.6 Hz), 144.2 (d,  $J = 23.9$  Hz), 134.5, 132.5 (d,  $J = 11.9$  Hz), 131.6, 129.7 (d,  $J = 13.3$  Hz), 126.0 (d,  $J = 80.3$  Hz), 120.6, 61.8. <sup>31</sup>P NMR (160 MHz in DMSO-d<sub>6</sub>): δ 62.6.

X-ray quality single crystals of **5** were obtained from ion exchange of **5** with NH<sub>4</sub>PF<sub>6</sub> to give the hexafluorophosphate salt of **5** (**5'**).

**Synthesis of Dichloro(η<sup>6</sup>-benzene){[3,5-bis(diphenylphosphinothioyl)pyridine-C<sup>4</sup>,S,S']}chloropalladium(II)} ruthenium(II) (6)**

To a THF (5 mL) solution of **2a** (9.8 mg, 0.015 mmol) was added [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>] (10.0 mg, 0.020 mmol), and refluxed for 12 h. The solvent was evaporated, and the residue was washed with ether and hexane. The product was purified by recrystallization from CHCl<sub>3</sub> to give a pale brown powder of **6** (8.8 mg, 65% yield). FAB-mass :  $m/z = 866$  [M-Cl]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>): δ 8.46 (dd,  $J = 5.3$  Hz, 2.2 Hz, 2H), 7.90-7.80 (m, 8H), 7.70-7.50 (m, 12H), 5.43 (s, 6H). <sup>31</sup>P NMR (160 MHz in CDCl<sub>3</sub>): δ 56.2. Anal. Calcd for C<sub>35</sub>H<sub>28</sub>Cl<sub>3</sub>NP<sub>2</sub>PdRuS<sub>2</sub>: C, 46.58; H, 3.13; N, 1.55. Found: C, 45.74; H, 2.78; N, 1.50. Because of low solubility of **6** in CDCl<sub>3</sub>, satisfactory <sup>13</sup>C NMR spectrum has not been obtained.

**Synthesis of Dichloro(benzonitrile){[3,5-bis(diphenylphosphinothioyl)pyridine-C<sup>4</sup>,S,S']}chloropalladium(II)} platinum(II) (7)**

To a THF (5 mL) solution of **2a** (9.8 mg, 0.015 mmol) was added PtCl<sub>2</sub>(PhCN)<sub>2</sub> (7.1 mg, 0.015 mmol), and stirred for 12 h. The solvent was evaporated, and the residue was washed with water, CH<sub>3</sub>CN, and ether. The product was purified by recrystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN to give a yellow powder of **7**

(5.1 mg, 33% yield).

FAB-mass :  $m/z = 1020$   $[M+H]^+$ .  $^1\text{H}$  NMR (400 MHz in  $\text{CDCl}_3$ ):  $\delta$  8.28 (dd,  $J = 5.6$  Hz, 1.7 Hz, 2H), 7.88-7.80 (m, 8H), 7.74-7.68 (m, 7H), 7.65-7.58 (m, 8H), 7.53 (dd,  $J = 8.2$  Hz, 7.0 Hz, 2H).  $^{31}\text{P}$  NMR (160 MHz in  $\text{CDCl}_3$ ):  $\delta$  56.1. Because of low solubility of **7** in  $\text{CDCl}_3$ , satisfactory  $^{13}\text{C}$  NMR spectrum has not been obtained. IR (KBr,  $\text{cm}^{-1}$ ): 2288 ( $\nu(\text{C}\equiv\text{N})$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{27}\text{Cl}_3\text{N}_2\text{P}_2\text{PdPtS}_2$ : C, 42.33; H, 2.66; N, 2.74. Found: C, 42.03; H, 2.98; N, 2.68.

#### X-ray Crystallographic Study.

The diffraction data were collected with a Rigaku Saturn CCD area detector with graphite monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71070$  Å) at  $-160$  °C. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods (SIR 2002) and expanded using Fourier techniques. In general, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

For **2a**, a solved  $\text{CHCl}_3$  molecule was located by using a rigid group due to disordering. For **6**, hydrogen atoms excepted for those of the  $\eta^6$ -benzene were refined using the riding model due to disordering.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; publication numbers CCDC 659442 (**1**), 659443 (**2a**· $2\text{CHCl}_3$ ), 659444 (**2b**· $2\text{CHCl}_3$ ), 659445 (**2c**· $\text{CHCl}_3$ ), 659446 (**3'**· $2\text{CH}_3\text{CN}$ ), 659447 (**5'**· $\text{CH}_3\text{CN}$ ), 659448 (**6**· $\text{CHCl}_3$ ).

Figures giving ORTEP drawings of **2b** and **2c**, and UV-vis spectra of the complexes are provided as Supplementary material. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2007.08.026](https://doi.org/10.1016/j.jorgchem.2007.08.026).

**Acknowledgement**

The authors are grateful to Prof. K. Tanaka, Dr. R. Okamura, and Ms. K. Tsutsui of Institute for Molecular Science for ESI-MS measurement.

## References

1. (a) M. Albrecht, G. van Koten, *Angew. Chem. Int. Ed.* 40 (2001) 3750. (b) P. Steenwinkel, R. A. Gossage, G. van Koten, *Chem. Eur. J.* 4 (1998) 759. (c) M. van der Boom, D. Milstein, *Chem. Rev.* 103 (2003) 1759. (d) J. T. Singleton, *Tetrahedron* 59 (2003) 1837. (e) K. J. Szabó, *Synlett* (2006) 811, and references therein.
2. (a) C. H. M. Amijs, G. P. M. van Klink, G. van Koten, *Dalton Trans.* (2006) 308. (b) F. Würthner, C.-C. You, C. R. Saha-Möller, *Chem. Soc. Rev.* 33 (2004) 133. (c) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.* 43 (2004) 2334. (d) M. Fujita, *Chem. Soc. Rev.* 27 (1998) 417, and references therein.
3. (a) M. Q. Slagt, G. Rodríguez, M. M. P. Grutters, R. J. M. Klein Gebbink, W. Klopper, L. W. Jenneskens, M. Lutz, A. L. Spek, G. van Koten, *Chem. Eur. J.* 10 (2004) 1331. (b) R. van de Coevering, M. Kuil, A. P. Alfers, T. Visser, M. Lutz, A. L. Spek, R. J. M. Klein Gebbink, G. van Koten, *Organometallics* 24 (2005) 6147. (c) A. V. Chuchuryukin, P. A. Chase, H. P. Dijkstra, B. M. J. M. Suijkerbuijk, A. M. Mills, A. L. Spek, G. P. M. van Klink, G. van Koten, *Adv. Synth. Catal.* 347 (2005) 447. (d) C. H. M. Amijs, G. P. M. van Klink, M. Lutz, A. L. Spek, G. van Koten, *Organometallics* 24 (2005) 2944. (e) J. R. Hall, S. J. Loeb, G. K. H. Shimizu, G. P. A. Yap, *Angew. Chem. Int. Ed.* 37 (1998) 121. (f) H.-J. van Manen, R. H. Fokkens, van F. C. J. M. Veggel, D. N. Reinhoudt, *Eur. J. Org. Chem.* (2002) 3189. (g) S. Back, M. Albrecht, A. L. Spek, G. Rheinwald, H. Lang, G. van Koten, *Organometallics* 20 (2001) 1024. (h) S. Back, R. A. Gossage, H. Lang, G. van Koten, *Eur. J. Inorg. Chem.* (2000) 1457. (i) S. Back, M. Lutz, A. L. Spek, H. Lang, G. van Koten, *J. Orgnomet. Chem.* 620 (2001) 227. (j) P. Steenwinkel, D. M. Grove, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* 17 (1998) 5647. (k) M. Gagliardo, G. Rodríguez, H. H. Dam, M. Lutz, A. L. Spek, R. W. A. Havenith, P. Coppo, L. D. Cola, F. Hartl, G. P. M. van Klink, G. van Koten, *Inorg. Chem.* 45 (2006) 2143. (l) B. M. J. M. Suijkerbuijk, M. Lutz, A. L. Spek, G. van Koten, R. J. M. Klein Gebbink, *Org. Lett.* 6 (2004) 3023. (m) W. C. Yount, H. Juwarker, S. L. Craig, *J. Am. Chem. Soc.* 125 (2003) 15302. (n) W. W. Gerhardt, A. J. Zuccherro, J. N. Wilson, C. R. South, U. H. F. Bunz, M. Weck, *Chem. Commun.* (2006) 2141. (o) C. H. M. Amijs, A. Berger, F. Soulimani, T. Visser, G. P. M. van Klink, M. Lutz, A. L. Spek, G. van Koten, *Inorg.*

- Chem. 44 (2005) 6567. (p) S. J. Loeb, G. K. H. Shimizu, J. A. Wisner, *Organometallics* 17 (1998) 2324. (q) S. J. Loeb, G. K. H. Shimizu, *J. Chem. Soc., Chem. Commun.* (1993) 1395. (r) M. Gagliardo, J. Perelaer, F. Hartl, G. P. M. van Klink, G. van Koten, *Eur. J. Inorg. Chem.* (2007), 2111. (s) G. D. Batema, K. T. L. van de Westelaken, J. Guerra, M. Lutz, A. L. Spek, C. A. van Walree, C. de Mello Donegá, A. Meijerink, G. P. M. van Klink, G. van Koten, *Eur. J. Inorg. Chem.*, 2007, 1422.
4. (a) T. Kanbara, T. Yamamoto, *J. Organomet. Chem.* 688 (2003) 15. (b) T. Kanbara, T. Yamamoto, *Focus on Organometallic Chemistry Research*; Cato, M. A. Ed., Nova Science Publishers; New York (2005) 111. (c) J. Fischer, M. Schürmann, M. Mehring, U. Zachwieja, K. Jurkschat, *Organometallics* 25 (2006) 2886. (d) O. Piechaczyk, T. Cantat, N. Mézailles, P. Le Floch, *J. Org. Chem.* 72 (2007) 4228.
5. (a) A. Weisman, M. Gozin, H.-B. Kraatz, D. Milstein, *Inorg. Chem.* 35 (1996) 1792. (b) M.-C. Lagunas, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *Eur. J. Inorg. Chem.* (1998) 163. (c) T. Koizumi, T. Tomon, K. Tanaka, *Bull. Chem. Soc. Jpn.* 76 (2003) 1969.
6. (a) O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* 522 (1996) 69. (b) P. Machnitzki, T. Nickel, O. Stelzer, C. Landgrafe, *Eur. J. Inorg. Chem.* (1998) 1029. (c) T. Kanbara, S. Takase, K. Izumi, S. Kagaya, K. Hasegawa, *Macromolecules* 33 (2000) 657. (d) T. Kanbara, S. Takase, R. Hayashi, S. Kagaya, K. Hasegawa, T. Yamamoto, *J. Polym. Sci.: Part A: Polym. Chem.* 40 (2002) 2637. (e) Z. Jin, B. L. Lucht, *J. Organomet. Chem.* 653 (2002) 167. (f) A. L. Schwan, *Chem. Soc. Rev.* 33 (2004) 218. (g) Z. Jin, B. L. Lucht, *J. Am. Chem. Soc.* 127 (2005) 5586.
7. (a) M. Doux, L. Ricard, P. Le Floch, N. Mézailles, *Dalton Trans.* (2004) 2593. (b) M. Doux, N. Mézailles, L. Ricard, P. Le Floch, *Eur. J. Inorg. Chem.* (2003) 3878.
8. (a) B. Crociani, F. Di Bianca, A. Giovenco, *J. Organomet. Chem.* 251 (1983) 393. (b) M. Albrecht, H. Stoeckli-Evans, *Chem. Commun.* (2005) 4705. (c) N. A. Piro, J. S. Owen, J. E. Bercaw, *Polyhedron* 23 (2004) 2797.
9. W. H. Meyer, M. Deetlefs, M. Pohlmann, R. Scholz, M. W. Esterhuysen, G. R. Julius, H. G. Raubenheimer,

Dalton Trans. (2004) 413.

10. O. Schuster, H. G. Raubenheimer, *Inorg. Chem.* 45 (2006) 7997.
11. L. Carter, D. L. Davies, J. Fawcett, D. R. Russell, *Polyhedron* 12 (1993) 1123.
12. H. Jude, J. A. K. Bauer, W. B. Connick, *Inorg. Chem.* 41 (2002) 2275.
13. J. R. Doyle, P. E. Slade, H. B. Jonassen, *Inorg. Synth.* 6 (1960) 216.
14. P. Braunstein, R. Bender, J. Jud, *Inorg. Chem.* 26 (1989) 341.



### Captions of Figures

**Figure 1.** X-ray crystal structures of (a) **1** and (b) **2a** with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms and solvated  $\text{CHCl}_3$  molecules are omitted for simplicity.

**Figure 2.** X-ray crystal structures of (a) **3'** and (b) **5'** with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms, an  $\text{PF}_6^-$  anion, and solvated  $\text{CH}_3\text{CN}$  molecules are omitted for simplicity.

**Figure 3.** X-ray crystal structure of **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and a solvated  $\text{CHCl}_3$  molecule are omitted for simplicity.

**Table 1.** Crystal data and details of the structure refinements for **1**, **2a**, **3'**, **5'**, and **6**

	<b>1</b>	<b>2a</b> ·2CHCl <sub>3</sub>	<b>3'</b> ·2CH <sub>3</sub> CN	<b>5'</b> ·CH <sub>3</sub> CN	<b>6</b> ·CHCl <sub>3</sub>
formula	C <sub>29</sub> H <sub>23</sub> NP <sub>2</sub> S <sub>2</sub>	C <sub>31</sub> H <sub>24</sub> Cl <sub>7</sub> NP <sub>2</sub> PdS <sub>2</sub>	C <sub>34</sub> H <sub>31</sub> F <sub>6</sub> IN <sub>3</sub> P <sub>3</sub> PdS <sub>2</sub>	C <sub>34</sub> H <sub>30</sub> BrF <sub>6</sub> N <sub>2</sub> P <sub>3</sub> PdS <sub>2</sub>	C <sub>36</sub> H <sub>29</sub> Cl <sub>8</sub> NP <sub>2</sub> PdRuS <sub>2</sub>
mol wt	511.57	891.18	985.98	923.96	1021.89
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space Group	C2/c (No.15)	P2 <sub>1</sub> /c (No.14)	Pbar (No.2)	P2 <sub>1</sub> /n (No.14)	P2 <sub>1</sub> /n (No.14)
<i>a</i> /Å	13.294(5)	9.2258(17)	7.284(3)	9.626(3)	12.026(7)
<i>b</i> /Å	16.697(6)	22.234(3)	12.362(5)	14.511(4)	29.677(14)
<i>c</i> /Å	12.912(5)	17.281(2)	22.099(10)	25.792(7)	12.007(6)
$\alpha^\circ$			86.366(15)		
$\beta^\circ$	113.683(5)	105.338(7)	88.584(14)	92.426(3)	111.341(9)
$\gamma^\circ$			73.184(12)		
<i>V</i> / Å <sup>3</sup>	2624.6(17)	3418.6(9)	1901.0(13)	3599.7(16)	3992(4)
<i>Z</i>	4	4	2	4	4
$\mu/\text{cm}^{-1}$	3.43	13.311	15.958	19.384	14.432
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.295	1.731	1.722	1.705	1.7
no. unique reflns	2670	7612	7684	8204	9054
no. reflns measd	2227	6349	5631	4174	6637
			(>1.00σ( <i>I</i> ))		(>1.00σ( <i>I</i> ))
no. variables	169	391	482	472	465
<i>R</i> <sub>1</sub>	0.0426	0.112	0.0441	0.0434	0.1398
	(>2.00σ( <i>I</i> ))	(>2.00σ( <i>I</i> ))	(>1.00σ( <i>I</i> ))	(>2.00σ( <i>I</i> ))	(>1.00σ( <i>I</i> ))
<i>R</i> <sub>w</sub>	0.0595	0.1392	0.0592	0.0487	0.1069
	(>2.00σ( <i>I</i> ))	(>2.00σ( <i>I</i> ))	(>1.00σ( <i>I</i> ))	(>2.00σ( <i>I</i> ))	(>1.00σ( <i>I</i> ))
GOF	1.066	1.341	0.875	0.836	0.996

**Table 2.** Selected bond lengths (Å) for **1**, **2a**, **3'**, **5'**, and **6**

Bond length (Å)					
	<b>1</b>	<b>2a</b>	<b>3'</b>	<b>5'</b>	<b>6</b>
Pd–C <sub>ipso</sub>		1.964(9)	1.994(6)	1.994(5)	1.999(12)
Pd–halogen		2.390(2)	2.6661(7)	2.4843(8)	2.399(3)
Pd–S		2.355(2)	2.3305(16)	2.3098(18)	2.355(4)
Pd–S		2.344(2)	2.3277(16)	2.3217(17)	2.399(3)
P–S	1.9460(10)	2.003(3)	2.018(2)	2.010(2)	2.006(4)
P–S	1.9460(10)	2.012(3)	2.008(2)	2.004(2)	2.018(3)
C( $\beta_{py}$ )–P	1.814(2)	1.810(9)	1.808(5)	1.809(6)	1.784(14)
C( $\beta_{py}$ )–P	1.814(2)	1.793(7)	1.822(6)	1.794(6)	1.784(13)
N <sub>py</sub> –C(sp <sup>3</sup> ) <sup>a</sup>			1.502(9)	1.502(8)	
N <sub>py</sub> –Ru					2.152(8)
Ru–Cl					2.408(3)
Ru–Cl					2.411(4)

<sup>a</sup> N<sub>py</sub>-quaternized substituent of **3'** and **5'**.

**Table 3** UV-vis absorption spectroscopic data for **1-8**<sup>a</sup>

absorption	
$\lambda_{\text{max}}$ / nm ( $\epsilon \times 10^{-3}$ / M <sup>-1</sup> cm <sup>-1</sup> )	
<b>1</b>	255 (29.8), 295 (5.8)
<b>2a</b>	263 (30.4), 301 (6.4), 346 (1.7)
<b>2b</b>	263 (33.6), 309 (5.4), 352 (1.8)
<b>2c</b>	262 (33.9), 309 (11.6), 392 (2.0)
<b>3</b>	361 (28.5), 370 (7.8), 405 (3.1)
<b>4</b>	257 (38.2), 324 (6.6), 367 (4.7)
<b>5</b>	254 (31.1), 324 (5.6), 363 (3.9)
<b>6</b>	262 (33.0), 302 (12.4), 405 (1.5)
<b>7</b>	264 (35.0), 304 (13.6), 400 (1.1)
<b>8</b> <sup>b</sup>	265 (3.1), 323 (5.5)

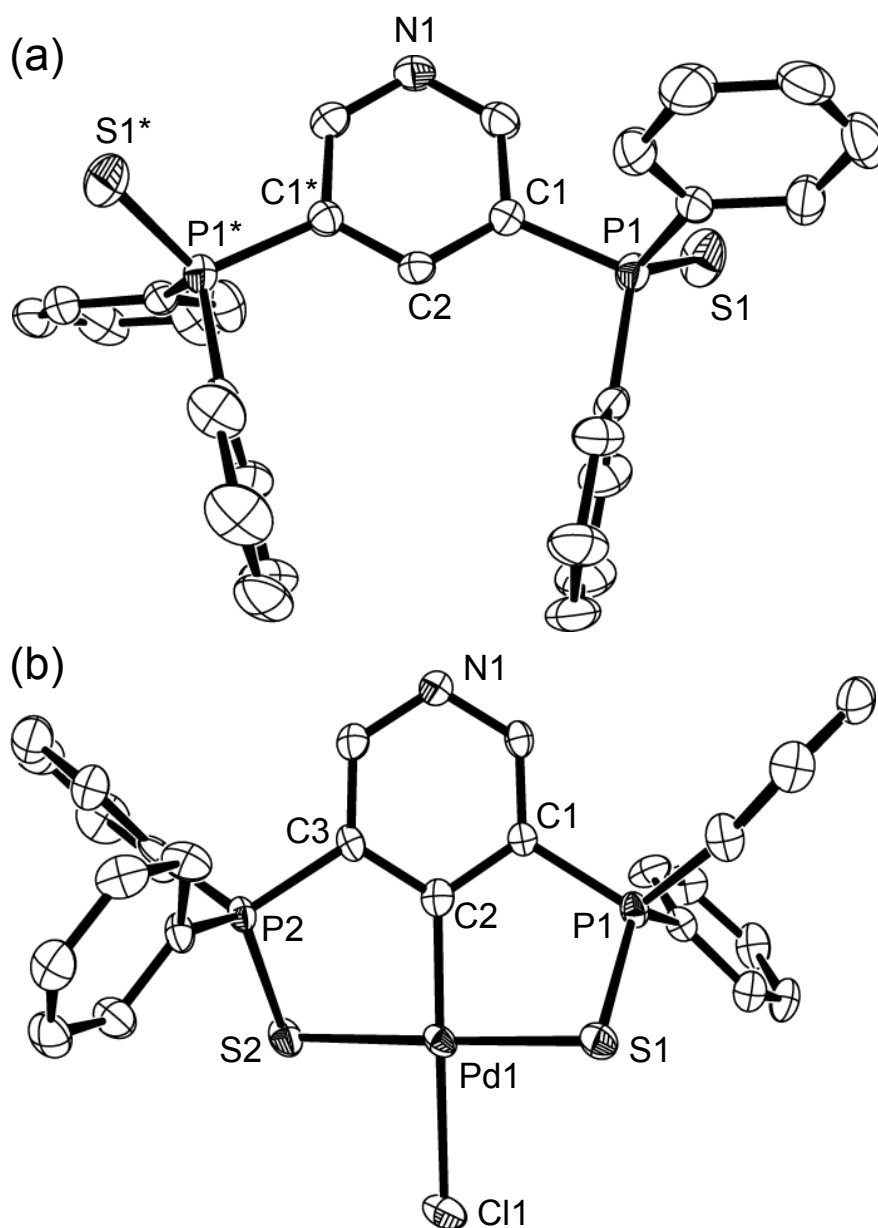
<sup>a</sup> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>b</sup> from ref. 4a and 4b.

**Table S1.** Crystal data and details of the structure refinements for **2b** and **2c**

	<b>2b</b> ·2CHCl <sub>3</sub>	<b>2c</b> ·CHCl <sub>3</sub>
formula	C <sub>31</sub> H <sub>24</sub> BrCl <sub>6</sub> NP <sub>2</sub> PdS <sub>2</sub>	C <sub>30</sub> H <sub>23</sub> Cl <sub>3</sub> INP <sub>2</sub> PdS <sub>2</sub>
mol wt	935.63	863.25
cryst syst	monoclinic	monoclinic
space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No.14)	<i>P</i> 2 <sub>1</sub> / <i>a</i> (No.14)
<i>a</i> /Å	9.312(5)	17.415(4)
<i>b</i> /Å	22.653(12)	10.653(2)
<i>c</i> /Å	17.383(10)	18.116(4)
$\alpha$ <sup>o</sup>		
$\beta$ <sup>o</sup>	105.279(7)	109.867(3)
$\gamma$ <sup>o</sup>		
<i>V</i> / Å <sup>3</sup>	3537(3)	3160.7(11)
<i>Z</i>	4	4
$\mu$ /cm <sup>-1</sup>	23.442	20.742
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.757	1.814
no. unique reflns	8030	7182
no. reflns measd	4458	4455
	( <i>I</i> >1.00σ( <i>I</i> ))	
no. variables	421	384
<i>R</i> <sub>1</sub>	0.0905	0.0384
	( <i>I</i> >1.00σ( <i>I</i> ))	( <i>I</i> >2.00σ( <i>I</i> ))
<i>R</i> <sub>w</sub>	0.0896	0.0472
	( <i>I</i> >1.00σ( <i>I</i> ))	( <i>I</i> >2.00σ( <i>I</i> ))
GOF	0.917	0.906

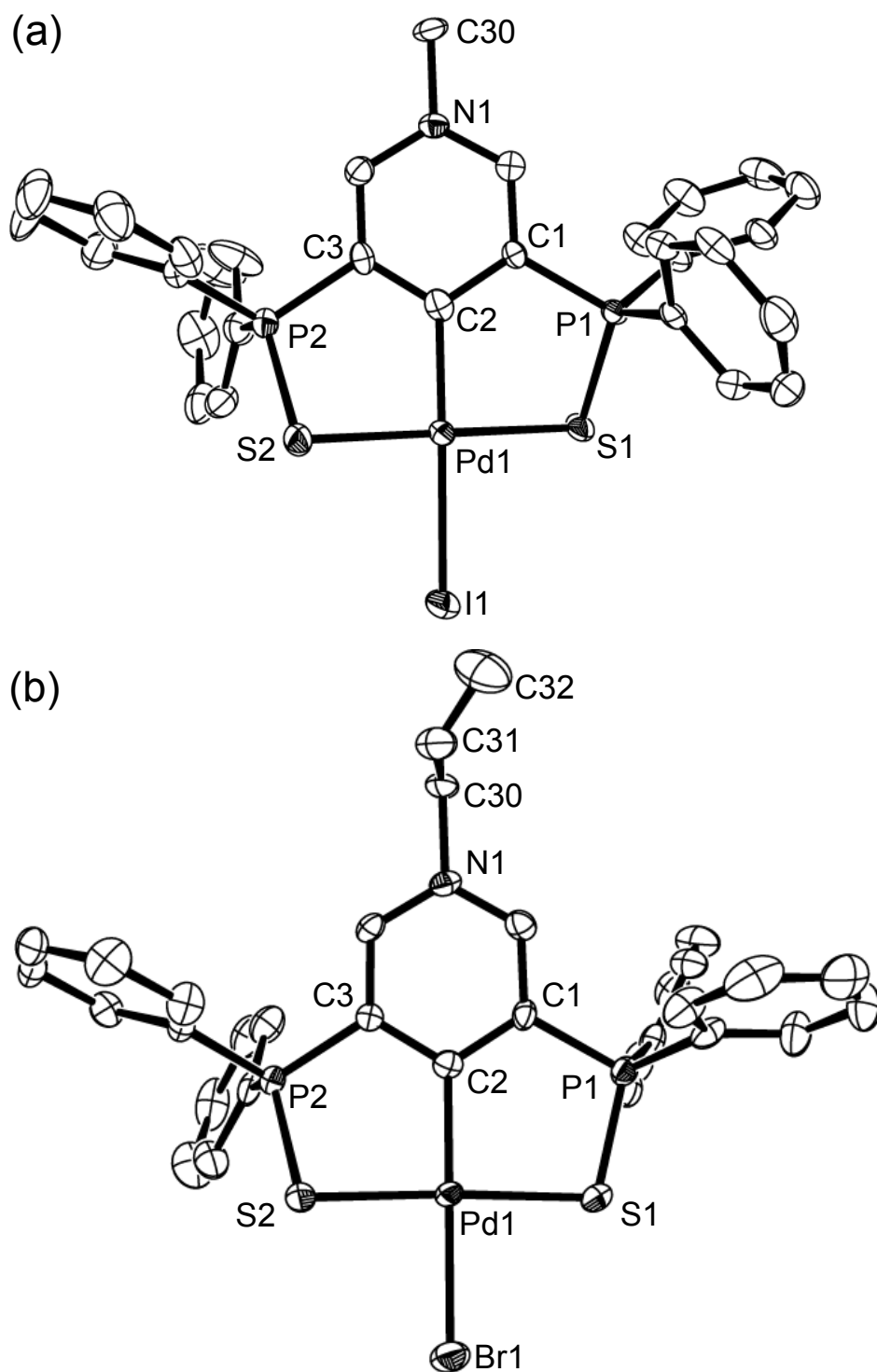
**Table S2.** Selected bond lengths for **2b** and **2c**

	<b>2b</b>	<b>2c</b>
Pd–C <sub>ipso</sub>	2.006(11)	2.005(5)
Pd–halogen	2.5062(18)	2.6797(6)
Pd–S	2.352(3)	2.3188(15)
Pd–S	2.345(3)	2.3098(15)
P–S	2.006(4)	2.016(2)
P–S	2.021(5)	2.007(2)
C(β <sub>py</sub> )–P	1.803(12)	1.800(5)
C(β <sub>py</sub> )–P	1.809(10)	1.785(5)



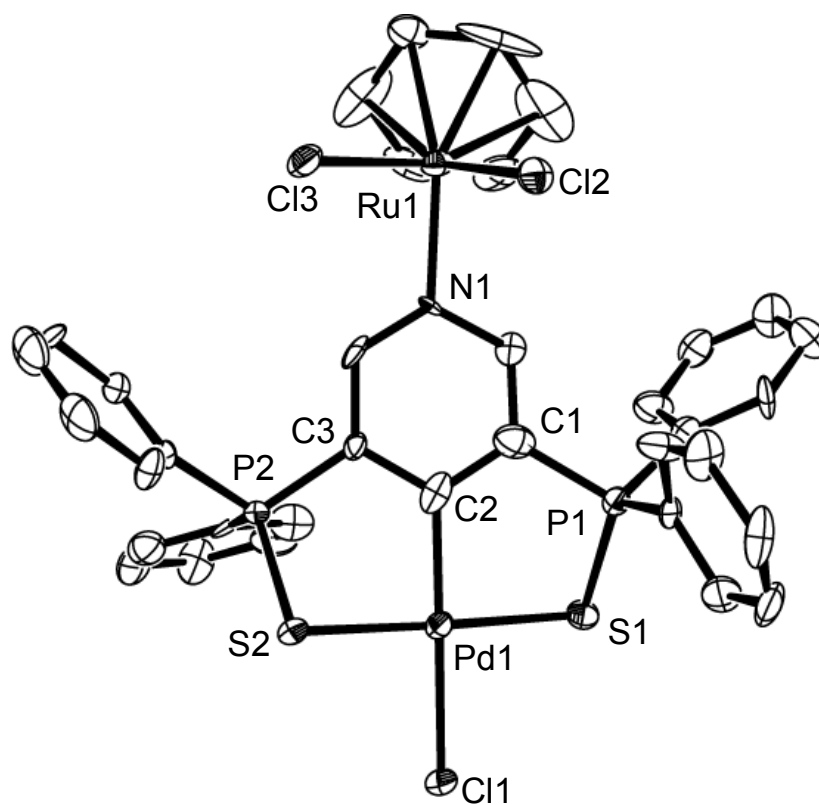
**Figure 1.** X-ray crystal structures of (a) **1** and (b) **2a** with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms and solvated  $\text{CHCl}_3$  molecules are omitted for simplicity.



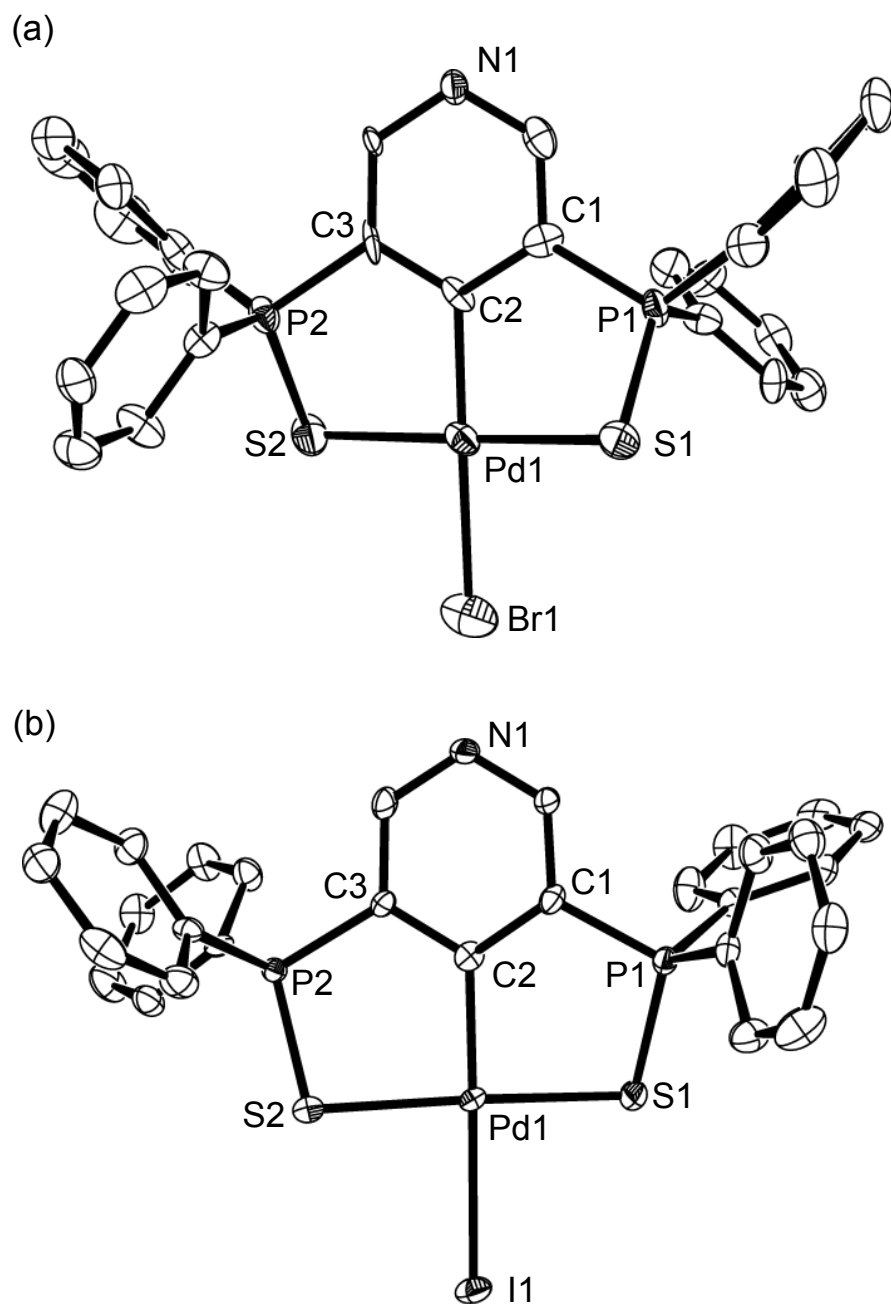
**Figure 2.** X-ray crystal structures of (a) **3'** and (b) **5'** with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms, an  $\text{PF}_6^-$  anion, and solvated  $\text{CH}_3\text{CN}$  molecules are omitted for simplicity.

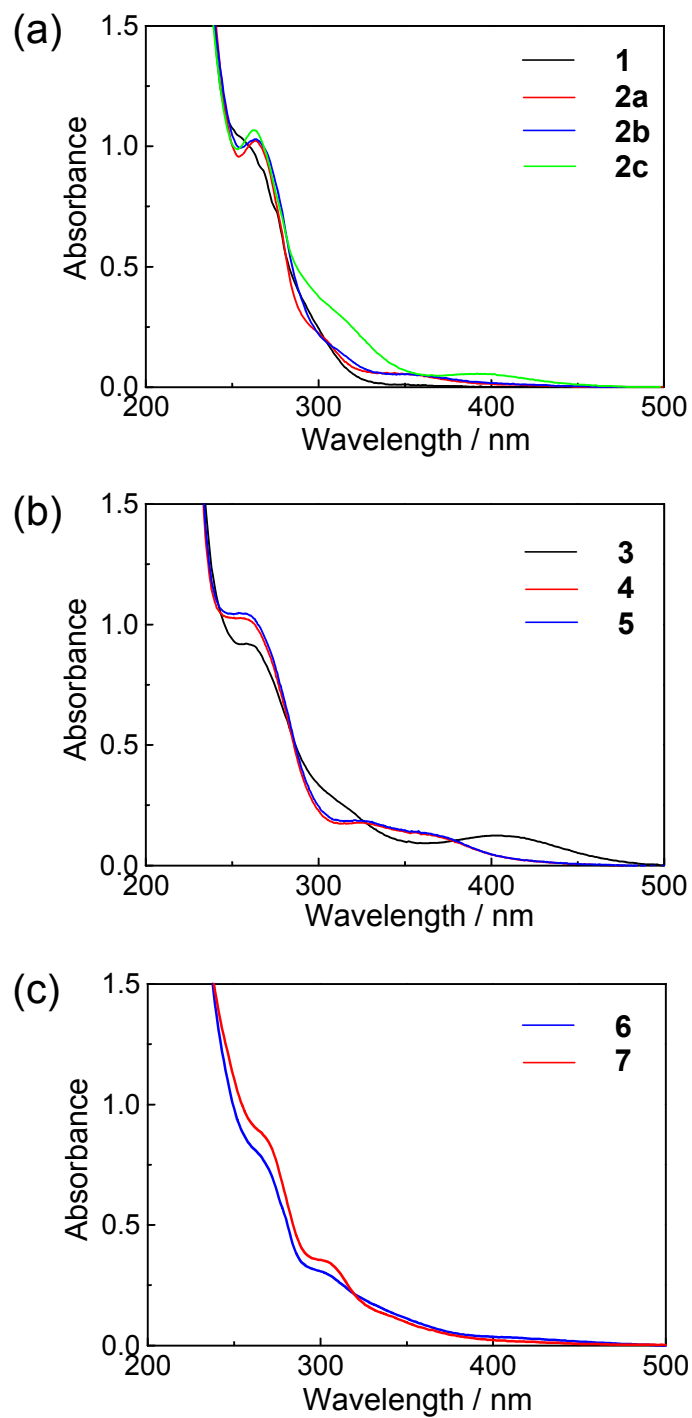


**Figure 3.** X-ray crystal structure of **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and a solvated  $\text{CHCl}_3$  molecule are omitted for simplicity.





**Figure S1.** X-ray crystal structures of (a) **2b** and (b) **2c** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvated  $\text{CHCl}_3$  molecules are omitted for simplicity.



**Figure S2.** UV-vis absorption spectra of the ligands and the complexes in  $\text{CH}_2\text{Cl}_2$  at room temperature: (a) **1** and **2a-c**, (b) **3**, **4**, and **5**, (c) **6** and **7**.

**Corresponding author: Takaki Kanbara**

Graduate School of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

Tel.: +81-29-853-5066; fax: +81-29-853-4490; E-mail: kanbara@ims.tsukuba.ac.jp

**Graphical Abstract**

Title: Synthesis, Structure, and Quaternization and Complexation Reactions of  $\kappa^3\text{SCS}$  Pincer Palladium Complexes Having 3,5-Pyridinediyl Unit

Authors: Hikaru Meguro<sup>a</sup>, Take-aki Koizumi<sup>a</sup>, Takakazu Yamamoto<sup>a</sup>, and Takaki Kanbara<sup>b,c,\*</sup>

Address: <sup>a</sup>Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

<sup>b</sup>Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

<sup>c</sup>Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

Abstract: The cyclopalladation of 3,5-bis(diphenylphosphinothioyl)pyridine afforded new  $\kappa^3\text{S,C,S}$ -pincer palladium complexes with a  $\sigma$ -bond between Pd and 4-C of the centered 3,5-pyridinediyl unit. By utilizing the quaternization and complexation ability of the pyridine imine nitrogen ( $\text{N}_{\text{py}}$ ) atom, various new pincer-type complexes, including hetero-binuclear complexes, have been synthesized.

Keywords: Pincer complex; Palladium; Pyridine; Quaternization; Binuclear complexes

